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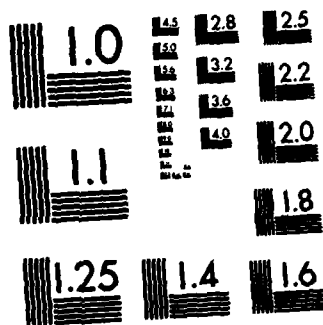
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The Electronics Technology Division requires understanding of their mission and related problems of novel phenomena and materials with unusual properties for possible device applications. Theoretical and numerical modeling was conducted to obtain a fundamental understanding of low frequency dynamic responses of condensed matter with emphasis on polymers, photoelectronic materials, semiconductor interfaces, amorphous metals and amorphous semiconductors.		

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1.0 INTRODUCTION

The work consisted of writing, modifying, and running computer programs in BASIC and Fortran and using these computer codes for theoretical modelling of the NRL theory of low frequency relaxation phenomenon. Data analysis performed included work on dynamics of entangled polymer melts, physical aging of glasses, dielectric relaxation near the glass transition, and transient luminescence, transport and photoconductivity in chalcogenide glasses. Specifically, the following physical problems were theoretically modelled and compared with experimental data.

2.0 POLYMER MELTS

Application of the NRL model to polymer melts provides a quantitative explanation for the viscoelastic properties of entangled polymer chains including $G(t)$, $G''(\omega)$, $G_n^* J_c^*$ and η as well as their molecular weight dependences. The model predicts simultaneously the temperature dependence of η as given approximately by the Vogel form and the shift factor a_T in the WLF form. Modelling is quantitatively successful for entangled linear as well as branched polymers.

3.0 PHYSICAL AGING

Aging effects are found to be contained in an increase in the NRL model parameter η as aging proceeds, resulting in a shift of the entire spectrum of relaxation times. The class of creep compliance functions corresponding to the NRL model relaxation modules turns out to naturally describe Andrade creep behaviour and at long times produces flow like behavior. The modelling allows quantitative comparisons with creep measurements on glasses, amorphous metals, and polymers.

4.0 Na β -ALUMINA

Frequency and temperature dependences of the dielectric response of the fast ionic conductor Na β -alumina is found to be described by the NRL model. In particular unusual properties in the region from 50 to 300K, in which a transition from a glass-like to a liquid like phase takes place now be understood by means of this modelling of Na β -alumina data.

5.0 TRANSPORT IN CHALCOGENIDE GLASSES

The chalcogenide glasses are the most thoroughly studied amorphous semiconductor systems. The transient transport data, transient optical data, dynamical dielectric relaxation data, and the volume and enthalpy recovery data of chalcogenide glasses are found to conform to the NRL model predictions. All the available data

has been analyzed, in particular the recent transient optical and transport data, allowing for the first time a clear distinction between predictions of various models. NRL model behavior is found in all cases and transport by small polaron hopping is confirmed.

6.0 PUBLICATIONS

The attached paper resulted from work done on the contract.



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STRESS RELAXATION AND LOSS MODULI MEASUREMENTS IN LINEAR
AND BRANCHED POLYMER SYSTEMS CORRELATED WITH STEADY STATE
VISCOSITY: MOLECULAR WEIGHT DEPENDENCES

by

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Nearly a decade ago, de Gennes¹ introduced the concept that entangled polymer chains relax by reptation. Doi and Edwards (DE)² have developed a model relating the dynamics of reptating chains to viscoelastic properties. They assumed that in polymer melts and solutions with chain entanglements, reptation would be the dominant motion. The stress relaxation modulus $G(t)$ in the terminal region has been given and from it the plateau modulus, the viscosity η and the recoverable compliance J_e^0 can be obtained together with their dependences on M_e . In particular ηM_e , in close agreement with the $\eta M_e^{3.4}$ law of large mol. wt. linear polymers. Acceptance of the de Gennes-DE model will follow confirmation of reptation by microscopic probes such as neutron scattering. Unfortunately, the results of a recent experiment³ designed for such a test fail to support the existence of reptation. Until reptation is confirmed we must be aware of it being at the present time an assumption only. The purpose of this work is to show that the fundamental mechanism (FM) behind a unified model (UM) of dynamical processes in condensed matter⁴ readily provides an explanation for the ηM_e dependence, as well as viscoelastic properties including $G(t)$, $G''(\omega)$, G'_0 and J_e^0 . The reptation assumption is not required. Besides, the same FM predicts simultaneously the temperature dependence of η as given approximately by the Vogel form, and the shift factor a_T in the WLF form.⁶ The reptation model does not address the temperature dependence problem at all. Moreover, the FM is applicable to both entangled linear and branched polymers, while the reptation model in its present form is inapplicable to branched polymers.

No coherent description of the FM and the UM will be attempted here. For details the reader is referred to Refs. 4-9. It has been shown that the relaxation rate τ_i^{-1} of a mode i is modified by the FM to be time dependent according to $\tau_i^{-1} \exp(-n_i \gamma) (\omega t)^{-n_i}$ where $\gamma=0.577$, ω is a cut-off frequency and n_i is the infrared divergence exponent with $0 \leq n_i < 1$. The rate equation for mode relaxation is modified from $dQ_i/dt = -(1/\tau_i) Q_i$ to $dQ_i/dt = -(1/\tau_i) \exp(-n_i \gamma) (\omega t)^{-n_i} Q_i$. The solution of which is $Q_i(t) = Q_i(0) \exp[-\exp(-n_i \gamma) t^{1-n_i}/(1-n_i) \tau_i \omega^{n_i}] \approx Q_i(0) \exp[-t/\tau_{pi}]^{1-n_i}$, which for $n_i \rightarrow 0$ reduces to $Q_i(0) \exp(-t/\tau_i)$. When $n_i \neq 0$ it is a fractional exponential and τ_i is shifted to

$$\tau_{pi} = [\exp(n_i \gamma) (1-n_i) \tau_i \omega^{n_i}]^{1/(1-n_i)} \quad (1)$$

This specific fractional exponential relaxation function being a consequence of a FM has led us to work out its unifying predictions in many fields and materials. We point out here the aforementioned shift from τ_i to τ_{pi} , which we shall in this work use to derive the ηM_e relation, etc., has been repeatedly tested and verified in other areas including electron transport^{4,5} in amorphous SiO_2 and chalcogenide glasses, ion transport in conductors,⁶ dielectric and structural relaxations near T_g for polymers and small molecule glasses,⁷ γ relaxation of bulk polycarbonate,⁸ volume recovery⁹ of PVAc, etc.

To start with consider the Rouse model. The Rouse internal modes are periodic functions of bead positions along the chain. The i -th mode has characteristic period equal to M/i and relaxation time $\tau_i = M^2 \zeta_0 / 6\pi^2 i^2 M_0 kT$ where M_0 is the monomer mol. wt. and ζ_0 is the friction coefficient. The lower modes govern the large scale motions and have the longest relaxation times. The Rouse model gives a good description of data on linear chain polymers of low mol. wt., with ηM_e for $M < M_e$. For longer chains, η is a much stronger function of M . For $M > M_e$, the $\eta M_e^{3.4}$ power dependence holds.

In some linear systems μ appears to be larger than 3.4. In branched systems, μ can be considerably larger especially at high mol. wts. The change in M dependence occurs smoothly as M varies. When M exceeds M_c a plateau region appears in $J(t)$, $G(t)$, $G'(w)$ and $G''(w)$. These M -dependences are a direct indication of chain entanglement which sets in when $M > M_c$ and gives rise to a temporary network structure due to interlooping of the chains. Thus the onset of entanglement introduces a coupling between chains. If M is the average mol. wt. between entanglements commonly defined through the plateau modulus by $M = \rho RT / G_c^0$, the number of entanglement couplings per molecule is $M/M_c - 1$. Internal Rouse modes with $i > M/2M_c \equiv i_c$ involve cooperative motions over distances smaller than the entanglement spacing. They are of sufficiently short range and are unaffected by entanglement coupling. In our model this implies the coupling of the $i > i_c$ Rouse modes to the correlated states^{4,9} in the polymer melt or solution cannot occur through the entanglement junctions and it is so weak that effectively $a_i = 0$ for all $i > i_c$ and they are unshifted. On the other hand, lower mode motions with $i < i_c$, which impose cooperations that extend beyond the entanglement spacing, are coupled via the entanglement junctions to the correlated states of the polymer system and have nonzero a_i values. These modes are slowed down and according to Eq. (1) their τ_i 's are shifted to the large τ_i values. This is because $w_i \tau_i \gg 1$ which follows from the expected size^{4,9} of w_i and of the typical relaxation times in the plateau region and the terminal zone. The degree of cooperation is largest in the motion of the terminal relaxation mode $i=1$ and decreases as i increases. Hence a_i is maximum for $i=1$ and decreases as i increases towards i_c . The "gap" in the relaxation time spectrum between the other $i < i_c$ modes and the $i=1$ mode creates a plateau region. The gap is not a true gap, having some contributions from the higher i modes in the group $i < i_c$ that have smaller a_i and thus smaller shifts from τ_i to τ_i^e . In other words, since $a_1 > a_2 > \dots > a_{i_c} \rightarrow 0$, the shift $(\log \tau_i^e - \log \tau_i)$ is not uniform with respect to i . The transition region comprises an unshifted Rouse spectrum of $i > i_c$ modes. Each of the $i < i_c$ modes is individually shifted and modified to have the fractional exponential form of $\exp(-t/\tau_i^e)^{1-a_i}$. The τ_i now characterizes the time scale of the i -th non-exponential relaxation mode. The spacings between the τ_i 's are different, much more nonuniform and wider than the rigidly shifted Rouse spectrum.¹⁰ This can be seen from Eq. (1) as due to the $(1-a_i)^{-1}$ power and that $a_1 > a_2 > \dots > a_{i_c} \rightarrow 0$. The resulting spectrum, even though individual components are nonexponential, is much narrower than the rigidly shifted Rouse spectrum as we shall see later. Recall that $\tau_i \propto M^2$ for all i . However, for $i < i_c$, τ_i is shifted to τ_i^e which now varies as $M^{2/(1-a_i)}$. Since $2/(1-a_i) \geq 2$ we see the pseudo-gap or the plateau region widens as M increases. The separation between τ_{i_c} and τ_{i_c+1} is much larger than that between τ_i and τ_{i+1} . Hence the terminal region is almost entirely due to τ_1 . τ_1 is proportional to $M^{2/(1-a_1)} \approx M^2$. Its contribution to viscosity η according to the Rouse model is $(\rho RT / M) \tau_1^{a_1}$. That the terminal relaxation time τ_{p1} and η have different M -dependences is not in agreement with experiment. This last failure is not surprising because the Rouse model should not be applicable in its original form at high mol. wts. Entanglement means the chain cannot execute all Rouse-like motions. Some spacial confinement such as the fixed tube used by DE is appropriate though the total suppression of sustained transverse motions in the tube model is unrealistic.¹¹ Nevertheless we consider next the chain in the tube and rederive all the results with our FM. The reader should realize that the tube model referred to here means only chain confinement by a tube and no reptation is invoked. In fact the thrust of this work is to show that, without the reptation hypothesis, the FM which has already explained many properties in other related and unrelated fields, once more satisfactorily accounts for the polymer melt properties when the chain is confined in a tube.

The development initially follows closely the works of DE and of Graessley¹¹ except we replace the reptation modes by our FM shifted fractional exponential relaxing Rouse modes with shifted τ_i for $i < i_c$. Configuration rearrangements in

the terminal zone are accomplished essentially by the $i=1$ mode. The relaxation modulus is given by $G(t) = G_N^0 \exp(-t/\tau_{pi})^{1-n_1}$ where G_N^0 is the plateau modulus given by $4\nu NkT/5$ and independent of M . The viscosity η and J_e^0 related to $G(t)$ by $\eta = \int_0^\infty G(t) dt$ and $J_e^0 = \eta^{-2} \int_0^\infty t G(t) dt$ can be calculated. We obtain $\eta = G_N^0 (1-n_1)^{-1} \Gamma(1/(1-n_1)) \tau_{pi}$ and $J_e^0 = (1/G_N^0) (1-n_1) \Gamma(2/(1-n_1)) / \Gamma^2(1/(1-n_1))$, where Γ is the Gamma function. For $n=0.5$, the product $J_e^0 G_N^0 = 3$, τ_{pi} and η both $\propto M^4$. For $n=0.4$, $J_e^0 G_N^0 = 2.04$, τ_{pi} and η both $\propto M^{3.3}$. The transition region again consists of the unshifted (i.e. $n=0$) Rouse modes for $i > i_1$. The plateau region has some contribution from the unevenly shifted (i.e. $n_1 > n_{i+1}$) Rouse modes $i=2, 3, \dots, i_1-1$ in a tube. The derivation of a rheological constitutive equation within the tube model by DE, and the predictions of stress-strain experiments which follow from this, is largely unaffected by our replacement of reptation dynamics by FM dynamics. This is due to the approximate factorizability of the time dependence and the strain dependence. Thus many of the successful rheological predictions of DE are carried over into our model while we also retain the advantages of the FM dynamics. We present finally the predictions of our model for both linear and branched polymers. The results are displayed in Figs. 1-4. The $G''(\omega)$ data and the predictions are both for the terminal zone. Note that for narrow distribution linear polystyrene melt (Fig. 1), the $G''(\omega)$ dispersion is well fitted by model prediction with $n=0.425$ which at the same time predicts both τ_{pi} and η should be $\propto M^{3.5}$ with $\mu = 2/(1-0.425) \approx 3.5$ in agreement with the observed $M^{3.5}$ behavior. For branched polymers (Fig. 2), the fit to $G''(\omega)$ demands a larger n_1 value of 0.7 which predicts that $\eta \propto M^{0.7}$ again in agreement with data in these branched polystyrenes at high mol. wts. The linear relaxation modulus $G(t)$ curves are our model predictions obtained from an unshifted Rouse spectrum for $i > i_1$, and for $i \leq i_1$ we chose n_i to rise linearly from zero value at $i=i_1$ to n_1 as i decreases towards unity. The fit to the $G(t)$ data of Fig. 3 for concentrated solution of polystyrene in Aroclor 1248 requires $n_1 = 0.475$ which implies that $\eta \propto M^{3.8}$ with $\mu = 2/(1-0.475) \approx 3.8$. On the other hand branched polystyrenes (Fig. 4) of lower mol. wt. than that in Fig. 2 requires $n_1 \sim 0.56$ to 0.61 which predicts $\mu \sim 4.5$ to 5.1 . Our model predicts that dispersion of the viscoelastic functions (determined by n_1) at the terminal region is correlated with the $\eta \propto M^\mu$ behavior via the relation $\mu = 2/(1-n_1)$ and the size of $J_e^0 G_N^0$ via the relation $J_e^0 G_N^0 = (1-n_1) \Gamma(2/(1-n_1)) / \Gamma^2(1/(1-n_1))$. For linear polymers, typically we find from dispersion that n_1 ranges between 0.4 to 0.5 for MPM. These n_1 values give $3.35 \leq \mu \leq 4$ and $2.5 \leq J_e^0 G_N^0 \leq 3$, all in agreement with data. For branched polymers, as determined from dispersion, n_1 typically has larger values which implies larger μ and $J_e^0 G_N^0$. When n_1 is a function of M , the model further predicts that both η and J_e^0 become M dependent. All these features are in remarkable agreement with data. Details and further implications of the model will be presented elsewhere.

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